2. Eisenberg, A., Ed., "Ions in Polymers", *Am. Chem. Soc.*, Washington, D.C., 1980.
3. D. G. Pieff, R. A. Weiss and R. D. Lundberg, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1503 (1982).
4. T. D. Gierke, G .E. Munn and F. C. Wilson, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1687 (1981).
5. R. A. Weiss, J. Lefelor, and H. Toriumi, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 661 (1983).
6. Ogumi, Z., Takehara, Z., and Yoshizawa, S., *J. Electrochem. Soc.-Electrochem. Sci., and Technol.*, **131**, 769 (1984).
7. N. E. Prieto and C. R. Martin, *J. Electrochem. Soc.-Electrochem. Sci. and Technol.*, **131**, 751 (1984).
8. D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **106**, 59 (1984).
9. F. J. Waller, *U. S. Patent* 4,414,409 (1983).
10. W. H.Kao and T. Kuwana, *J. Am. Chem. Soc.*, **106**, 473 (1984).
11. W. Siebourg, R. D. Lndberg, and R. W. Lenz, *Macromolecules*, **13**, 1013 (1980).
12. R. D. Lundberg and R. R. Philips, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1143 (1982).
13. V. D. Mattera, Jr. and W. M. Risen, Jr., *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 67 (1984).
14. W. M. Risen, Jr., *et al.*, *Amer. Chem. Soc. Symposium Series* **302**, (1986), and references there in.
15. I. W. Shim, V. D. Mattera, Jr., and W.M. Risen, Jr., *J. Catal.*, **94**, 531 (1985).
16. V. D. Mattera, Jr., P. J. Squattrito, and W. M. Risen, Jr., *Inorg. Chem.*, **23**, 3597 (1984).
17. H. S. Makowski, R. D. Lundberg, and G. H. Snigbal, *U. S. Patent*, 3,870,841 (1975).
18. C. Y. Liang and S. Krimm, *J. Polym. Sci.*, **27**, 241 (1958).
19. G. Zundel, "Hydration and Intermolecular Interaction", Academic, New York, 1969.
20. G. Kresze, E. Ropte, and B. Schrader, *Spectrochim. Acta.*, **21**, 1633 (1965).
21. E. Linder and G. Vitzthum, *Chem. Ber.* **102**, 4026 (1969).
22. B. Nyberg and R. Larsson, *Acta Chem. Scandina*, **27**, 63 (1973).
23. G. Newman and D.B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).
24. G. B. Rouse, A. J. Tsatsas, A. Eisenberg, and W.M. Risen, Jr., *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 81 (1979).
25. A. T. Tsatsas and W. M. Risen, Jr., *Chem. Phy. Lett.*, **7**, 354 (1970).
26. S. L. Peluso, A. T. Tsatsas, and W. M. Risen, Jr., *ONR Technical Report* 79-01(U.S.A.).
27. D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc.*(A), 1504 (1968).
28. K. Nakamoto, C. Udovich, and J. Takemoto, *J. Am. Chem. Soc.*, **92**, 3973 (1970).
29. Y. Kanamura and K. Nakamoto, *Inorg. Chem.*, **14**, 63 (1975).
30. "Electronic Structure and Magnetism of Inorganic Compounds: Specialist Periodical Reports", Vol. 1-5, The Chemical Society, Burlington House, London
31. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier Publishing Company, 1984.
32. B. N. Figgis, "Introduction to Ligand Fields", Interscience Publishers, 1966.
33. D. Sutton, "Electronic Spectra of Transition Metal Complexes", Mcgraw-Hill, London, 1968.
34. R. J. Young, "Introduction to Polymers" Chapmann and Hall, New York, 1981.
35. P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, London, 1953.
36. A. Eisenberg and M. King, "Ion Containing Polymers; Physical Properties and Structures", Academic, New York, 1977.
37. J. H. Gibbs, "In Modern aspects of the Vitreous state", J. D. Markenzie, Ed., Buttersworth, Washington, D.C. 1960.
38. R. A. Weiss, *J. Polym. Sci. Polm. Phys. Ed.*, **20**, 65 (1982).

Cross Interaction Constants As a Measure of the Transition State Structure (Part VI). Nucleophilic Substitution Reactions of Benzyl Chlorides with Anilines and Benzylamines

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Results of kinetic studies on the reactions of benzyl chlorides with anilines and benzylamines are reported. Analyses of the cross interaction constants relevant to the degree of bond formation, ρ_{XY} and λ_{XY}, are carried out. The magnitudes of the two parameters indicated that the degree of bond formation in the transition state is the typical of that expected for an S_N2 reaction, but the reactions with benzylamines appear to have a slightly less degree of bond formation compared with the reactions with anilines.

Introduction

The nucleophilic substitution (S_N) reaction of benzyl chlorides has been a subject of numerous studies[1] because of its mechanistic versatility[2]. Some of the reactions including solvolyses exhibited borderline behaviors[3] in the S_N1-S_N2

Table 1. Second Order Rate Constants, k_2($\times 10^4 M^{-1}sec^{-1}$) and the Hammett's ρ_X and ρ_Y and Brønsted Coefficients, β_X, for the reaction of Y-Benzyl Chlorides with X-Anilines in MeOH at 35.0°C[c]

Y X	p-CH$_3$	H	p-Cl	p-NO$_2$	$\rho_Y{}^b$
p-CH$_3$O	2.99	1.54	1.42	0.736	-0.41
p-CH$_3$	2.37	1.14	0.933	0.426	-0.53
H	1.48	0.585	0.468	0.179	-0.65
p-Cl	0.827	0.268	0.191	0.060	-0.80
$\rho_X{}^a$	-1.13	-1.54	-1.74	-2.19	
$\beta_X{}^a$	0.41	0.55	0.62	0.77	

[a] Correlation coefficient; r>0.997. [b] Correlation coefficient, r>0.999 for Y = H, p-Cl, p-NO$_2$. [c] k_2 values are averages of at least two determinations.

Table 2. Second Order Rate Constants, k_2($\times 10^{-4} M^{-1}sec^{-1}$) and the Hammett's ρ_X and ρ_Y, and Brønsted Coefficients, β_X, for the reactions of Y-Benzyl Chlorides with X-Benzylamines in MeCN at 55.0°C[c]

Y X	p-CH$_3$	H	p-Cl	p-NO$_2$	$\rho_Y{}^b$
p-CH$_3$O	16.8	14.5	13.5	10.7	-0.17
p-CH$_3$	14.4	12.1	11.0	8.51	-0.20
H	11.5	8.84	8.23	5.89	-0.26
p-Cl	8.51	6.17	5.50	3.72	-0.32
$\rho_X{}^a$	-0.60	-0.75	-0.80	-0.93	
$\beta_X{}^a$	0.57	0.73	0.75	0.89	

[a] Correlation coefficients; r>0.998. [b] Correlation coefficients; r>0.995 for Y = H, p-Cl, p-NO$_2$. [c] k_2 values are averages of at least two determinations.

Table 3. Cross Interaction Constants ρ_{XY} and λ_{XY} obtained by multiple linear regression of rate constants using eqs (1) and (3)

	ρ_X	ρ_Y	ρ_{XY}	cor coeff
AN	-1.61	-0.63	-0.75	0.999
BA	-0.75	-0.22	-0.22	0.999
	β_X	ρ_Y	λ_{XY}	
AN	0.56	-0.68	0.27	0.998
BA	0.73	-0.22	0.21	0.998

mechanistic spectrum rendering nonliner Hammett plots. In this respect, the transition state (TS) structure for the reaction has been, and still is, a center of interests for many physical organic chemists.

We have been engaged in the application of cross interaction constants, ρ_{ij}, β_{ij} and λ_{ij} defined in eqs 1-3, to the rationalization of mechanistic details involved in a variety of reactions[4].

$$\log (k_{ij}/k_{HH}) = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (1)$$

$$\log (k_{ij}/k_{HH}) = \beta_i \cdot \Delta pk_i + \beta_j \cdot \Delta pK_j + \beta_{ij} \cdot \Delta pK_i \cdot \Delta pK_j \quad (2)$$

$$\log (k_{ij}/k_{HH}) = \rho_i \sigma_i + \beta_j \cdot \Delta pK_j + \lambda_{ij} \sigma_i \cdot \Delta pK_j \quad (3)$$

We report here the results of our kinetic investigations of the nucleophilic substitution reactions of benzyl chlorides with anilines (AN) in methanol and with benzylamines (BA) in acetonitrile, Scheme 1. Our primary interest in this work is the characterization of the TS structure, in particular the degree of bond formation, with the use of relevant cross interaction constants, ρ_{XY} and λ_{XY}.

$$2XRNH_2 + YC_6H_4CH_2Cl \xrightarrow[\text{or MeCN}]{\text{MeOH}} YC_6H_4CH_2NHRX + {}^{+}NH_3RX + Cl^-$$

$R = C_6H_4$ or $C_6H_4CH_2$

$X = $ p-CH_3O, p-CH_3, H or p-Cl

$Y = $ p-CH_3, H, p-Cl or p-NO_2

Scheme 1

Results and Discussion

The second order rate constants, k_2, for the reactions of benzyl chlorides with AN in methanol at 35.0 °C and with BA in acetonitrile at 55.0 °C are summarized in Tables 1 and 2 respectively. For both AN and BA, an electron donating substituent in the nucleophile e.g., X = p-CH$_3$O, as well as in the substrate, e.g., Y = p-CH$_3$, is seen to enhance the reactivity. The reaction with the stronger nucleophile, BA, appears to be slightly faster than that with AN when a difference in reaction temperature is accounted for[5]. The signs of the simple Hammett's coefficients, ρ_X and ρ_Y, are both negative, indicating that bond breaking is ahead of bond formation in the TS. The magnitude of ρ_X is greater for the reactions with AN, the value being approximately twice of that for the reactions with BA. It is well known that in general the ρ value is reduced to nearly half[4j,6] when a nonconjugating intervening group, such as CH$_2$ in BA, is present in between the benzene ring and the reaction center, (N in BA); the magnitude of ρ_X, therefore, indicates nearly the same degree of change transfer from the nucleophiles AN and BA to the substrate suggesting a similar degree of bond formation. The magnitudes of the Brønsted's coefficient β_X($= \beta_N$) for the two reaction series with AN and BA also show little difference, (albeit they are slightly greater with BA), conforming to our findings of an approximately equal degree of bond formation based on the Hammett's coefficient ρ_X. Thus on both accounts, we may conclude that the degree of bond formation in the two reaction series is similar. On the other hand, a greater $|\rho_Y|$ for the AN series suggests that bond breaking of the C-Cl bond is greater for the AN series rather than for the BA series[7].

It is, however, often misleading to judge the degree of bond formation based solely on the simple Hammett, ρ, or Bronsted, β, coefficient as we have advocated time and again,[4e,f,j] especially when the comparison is made between two different reaction series as in the present work of reactions with AN and BA series. We do not expect the effect of solvent and temperature on the selectivity parameters ρ and β to be great, since the two solvent, MeOH and MeCN, can be regarded as isodielectric[8] and the difference in temperature is only 20 °C.[9]

We have determined the cross interaction constants ρ_{XY} and λ_{XY} by multiple linear regression of the rate constants k_2 using eqs (1) and (3) for the two reaction series and compared in Table 3. Reference to Table 3 indicates that the signs of the two constants agree between the two series but the magnitudes are different, especially $|\rho_{XY}|$ for the BA series is less than one third of that for the AN series. This is remarkable since we would have expected a difference of about a factor of two[6] considering an intervening CH_2 group in BA, if the degree of bond formation were similar for the two series. The markedly small $|\rho_{XY}|$ for the BA should therefore indicates an involvement of a greater distance between the two reaction centers in the substrate (α-carbon) and the nucleophile(N)[10], *i.e.*, a less degree of bond formation in the TS. This is further supported by a somewhat smaller $|\lambda_{XY}|$ value for the BA series (0.21) compared with that for the AN series (0.27). It is therefore convincing that the BA series proceeds via the S_N2 path with slightly less degree of bond formation in the TS relative to the AN series.

The actual magnitude of the two $|\lambda_{XY}|$ values are well within the range of those for the well-known S_N2 reaction series[4j] (0.20-0.27). It appears therefore that the reactions with BA have a TS which is somewhat earlier, *i.e.*, both bond formation and bond breaking has progressed less, than those with AN. This could mean that in the MeCN solvent, having less electrophilic pulling effect on the leaving group, bond breaking becomes less than that for the reactions in MeOH which has a greater electrophilic assistance for the leaving group, despite the similar bulk solvent (dielectric) property[8].

We conclude that the degree of bond formation in the TS for the reactions of benzyl chlorides with AN and BA is the typical of that expected for an S_N2 reaction, but the BA series seems to have somewhat less degree of bond formation and bond breaking.

Experimental

Materials. The solvents[4f], benzyl chlorides[1b], anilines[4f] and benzylamines[4j] were purified as needed by the methods described previously.

Reate Measurements. The rate was followed conductometrically. Pseudo-first-order rate constants, k_1^{obs}, determined by the Guggenheim method[11] was plotted against amine concentration, (eq 4) to obtain the second order rate constant k_2 from the slope. The methanolyses rate constant k_1 was negligible in all cases as evidenced by the zero inter-

$$k_1^{obs}=k_1+k_2\{\text{amine}\} \tag{4}$$

cept in the plot of eq 4. More than four amine concentrations were used, and the correlation coefficients of the plots were better than 0.998 in all cases. The rate constants k_2 were reproducible to within ±5%.

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References

1. (a) See for a review: A. Streitwieser. Jr, "Solvolytic Displacement Reaction", McGraw-Hill, New York, 1962, p. 18; (b) H. S. Golinkin, I. Lee and J. B. Hyne, *J. Am. Chem. Soc.*, **89,** 1307 (1967); (c) Y. J. Park and I. Lee, *J. Korean Chem. Soc.*, **9,** 23 (1965); (d) K. H. Jung, Y. Huh and I. Lee, *ibid.*, **9,** 148 (1965); (e) M. H. Whangbo, B. S. Lee and I. Lee, *ibid.*, **13,** 103 (1969); (f) I. Lee and J. B. Hyne, *Can. J. Chem.*, **47,** 1437 (1969); (g) M. H. Whangbo, B. S. Lee and I. Lee, *J. Korean Chem. Soc.*, **13,** 195 (1969); (h) I. Lee, B. S. Lee and J. E. Yie, *J. Korean Nucl. Soc.*, **3,** 198 (1971); (i) F. P. Ballistreri, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.*, **42,** 1415 (1977); (j) H. Aronovitch and A. Pross, *J. Chem. Soc. Perkin*, **2,** 540 (1978); (k) P. R. Young and W. P. Jencks, *J. Am. Chem. Soc.*, **101,** 3288 (1979); (l) J. A. Dodd and J. I. Brauman, *J. Phys. Chem.*, **90,** 3559 (1986).
2. N. S. Isaacs, "Physical organic Chemistry", Longman, Harlow, 1987, Chapter 10.
3. (a) D. J. Raber, J. M. Harris and P. V. R. Schleyer, in "Ions and Ion pairs in Organic Reactions" ed. M. Szwarc, John Wiley, New York, 1974, vol 2; (b) J. M. Harris, *Prog. Phys. Org. Chem.*, **11,** 89 (1974); (c) D. J. McLennan, *Accounts Chem. Res.*, **9,** 281 (1976).
4. (a) I. Lee, S. C. Sohn, *J. Chem. Soc. Chem. Commun*, 1055 (1986); (b) I. Lee, *Bull. Korean Chem. Soc.*, **8,** 426 (1987); (c) I. Lee, H. Y. Kim, H. K. Kang, *J. Chem. Soc. Chem. Commun.*, 1216 (1987); (d) I. Lee, *Bull. Korean Chem. Soc.*, **8,**200 (1987); (e) I. Lee and H. K. Kang, *Tetrahedron Lett.*, **28,** 1183 (1987); (f) I. Lee, H. K. Kang and H. W. Lee, *J. Am. Chem. Soc.*, **109,** 7472 (1987); (g) I. Lee, C. S. Shim, S. Y. Chung and H. W. Lee, *J. Chem. Soc. Perkin*, **2,** 975 (1988); (h) I. Lee, H. K. Kang, H. Y. Kim and H. W. Lee, *J. Org. Chem.*, **53,** 2678 (1988); (i) I. Lee, Y. H. Choi and H. W. Lee, *J. Chem. Soc. Perkin* **2,** 1537, 1988; (j) I. Lee, C. S. Shim, S. Y. Chung, H. Y. Kim and H. W. Lee, *J. Chem. Soc. Perkin* 2, In press; (k) I. Lee and I. C. Kim, *Bull. Korean Chem. Soc.*,**9,** 133 (1988); (l) I. Lee, C. S. Shim and I. C. Kim, *J. Phys. Org. Chem.*, In Press; (m) G. L. Han, J. H. Park and I. Lee, *Bull. Korean Chem. Soc.*, **8,** 393 (1987).
5. The rule of thumb gives a two fold increase in rate for the 10 °C increase in temperature.
6. R. D. Gillion, "Introduction to Physical organic Chemistry" Addison-Wesley, Reading, 1970, p. 146.
7. C. D. Johnson, "The Hammett Equation", Cambridge Univ. Press, Cambridge, 1973, p. 7.
8. The dielectric constants are 33.6 and 37.5 for MeOH and MeCN respectively at 20.0 °C: J. A. Dean, "Handbook of Organic Chemistry" McGraw-Hill, New York, 1987, Table 4-10.
9. The ten degree increase in the temperature changes ρ values ca. 5%[(6)].
10. I. Lee, *Bull. Korean Chem. Soc.*, **9,** 179 (1988).
11. E. A. Guggenheim, *Phil, Mag.*, **2,** 538 (1926).